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# Soil and Groundwater Remediation Proposal in an Aquifer of Venezuela by Hydrocarbon Transport Geostatistical Modeling

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#### Abstract

In this paper, it is presented a remediation proposal for soil and groundwater remediation proposal in an aquifer of Venezuela by hydrocarbon transport geostatistical modeling. The contamination with hydrocarbons is occurring in the northern region of an aquifer of the Carabobo State implying that the contaminants might be transported toward downstream of the aquifer causing an impact on the water for human consumption and industrial uses. The condition of the confined aquifer due to the alternating layers of low plasticity clay with well graded sand has avoided that the hydrocarbons in the soil reach a concentration that exceeds to the environmental regulation. For groundwater, the concentration of the hydrocarbons such as TPH, TPH-GRO, Lead, Benzene, Toluene, Ethylbenzene, m.Xylene, o.Xylene and MTBE is greater than to the environmental regulation. In most of cases, the spatial prediction of hydrocarbons is explained by local polynomial interpolation of orders between 2 and 3, and in minor proportion by global polynomial interpolation of orders between 2 and 3. The gradient of the linear regression function varies between 0.34 and 0.94. The proposal of remediation for hydrocarbons in soil and groundwater consists of applying of air injection and vapor extraction, requiring an estimated air injection of 13153 m<sup>3</sup>/d (323 cfm) and the vapor extraction of 5075  $m^3/d$  (125 cfm). The proposed wells for air injection (42) and vapor extraction (19) in a Carabobo State aguifer separated each 100 meters and 150 meters, respectively.

**Keywords:** Remediation, Groundwater, Spatial prediction model, Hydrocarbon transport

# **INTRODUCTION**

In this study, a remediation proposal for groundwater and soil derived from geostatistical modeling of hydrocarbon transport in an aquifer of Carabobo state, Venezuela, is presented. The aquifer is contained in an area where the main uses are urban and industrial. The source of pollution by hydrocarbons is a gas station located on one of the main highways, which connects the north-central region with the north-western region Venezuela, which causes a great demand for fuel services by this gas station. The objective of this document is to apply prediction spatial models using deterministic methods to analyze the distribution of hydrocarbons and propose a physical and chemical technology focused on achieving the of contaminants. The most removal chemical physical and common remediation technologies are pump and treat, in situ air sparging, in situ flushing and permeable reactive barriers (Darnault, 2008).

# **STUDY AREA**

The study area is an aquifer located in the Carabobo State, which is one of the states of Venezuela belonging to the northern region in front of the Caribbean sea



between the coordinates N 09°50'00", N 10°40'00", W67°30'00" and W68°20'00" (Figure 1). The aquifer is contained in an bounded the area bv following coordinates: N 10°05'30", N 10°11'00", W67°59'30" and W68°03'30". specific zone identified as the source of hydrocarbon contamination detected by GUACAOB community council due to the existence of strong fuel odors and the presence of fuel in rainwater collection channels and denounced to the local press and the Fire Department of Municipality of Valencia from August 2007; requesting investigation about its origin, it is a gas station known as "El Prado", which offers services to an industrial, commercial and residential uses in the Municipality of Valencia, Carabobo State. The investigation was started by the Civil Protection and Fire Department of Valencia Municipality, and the presence of volatile gases in a high degree was confirmed. In addition, the GUACAOB (Guacamaya-Caobos) community council spokespersons asked to the PDVSA-Yagua (Petroleos de Venezuela, S.A.) company the attention to the case. From August 2008, the GUACAOB Communal Council again denounced the annoyance due to the strong odor of fuel and the presence of free product in an excavation carried out for the construction of a water well, of a neighbor of the community. In September 2008, the Ministry of Energy and Petroleum (MEP) hires to the company Racing Oil Service 2021 of Venezuela on September 12, 2008 for applying tank tightness tests with the presence of the GUACAOB Community Council, detecting continuous pressure drop to zero (0) psi in a period of 20 minutes in the # 2 gasoline tank of 91

octane, which presented a fissure (leak). The MEP suspended the sale of fuel from this cracked tank. The rest of the petrol storage tanks of 91 octane (4 tanks), 95 octane (5 tanks) and diesel (three tanks) remained operational. The MEP did continuous monitoring in a house of the Los Caobos Urban District affected by the presence of fuel in a drainage. A sample is taken and analyzed in the Yagua Plant which resulted Laboratory, production of 91 octane gasoline. The MEP instructed the Concessionaire for the immediate characterization of soils to determine concentrations of Volatile Hydrocarbons and the extension of the pollutant plume and correct the damages caused to third parties. In October 2008, the Concessionaire built a new water well in the affected house of Urb. Los Caobos, however, it is presumed that the soil characterization was not carried out since the supports are not presented to MEP or PDVSA. No new claims from the community are presented. Between May 2014 and September 2015, It is reiterated to the concessionaire its noncompliance with the records of inventories, auditable records and the adequate collection of the data of the gauging, mechanical and electronic readings. In January 2016, members of the GUACAOB Community Council deliver a document to the District Management Department of the Gasoline Stations belonging the Yagua to Distribution Plant, requesting inspection of the houses located in the aforementioned residential complex as the neighbors complained of continuous strong odors to fuel, causing them discomfort and respiratory allergies especially children and older adults.



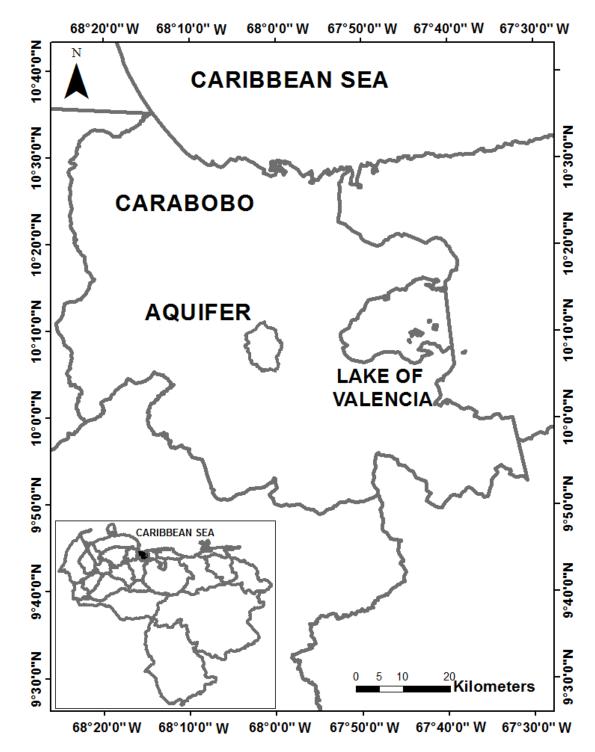


Fig: 1. Localization of the aquifer regarding to the Carabobo State, Venezuela

From January 2016, inspections to the El Prado gas station to evaluate the operating conditions and analyze the inventory controls and auditable records were required by MEP and PDVSA in order to detect if there were fuel leaks that show evidence of leakage. During these

inspections, it was evidenced that the Concessionaire carried out the replacement of a section of rigid petrol distribution pipe of 95 octanes without prior notification to PDVSA Company and MEP.

Between January and February 2016,



explosivity measurements were made in drainage channels of the Los Caobos community, where high values of these were found, presenting a dangerous combustible atmosphere, so a worktable was installed with all the organisms present such as PDVSA, MEP. Sales maintenance and Department, community of urbanization Los Caobos, Civil Protection and Fire Department, Ministry of Environment, Environment Department of the Mayor's Office of Valencia, to provide a solution to the problem. The actions taken were: a) Sampling of the fluid contained in the affected channel, b) tightness tests were made to pipes and volumetric tests to storage tanks for the El Prado gas station, c) Identification of other possible sources of pollution in the area (mechanical workshops, vehicle sales, production industries, d) temporary suspension of fuel sales service in the El Prado gas station as a prevention, until the tightness tests were carried out.

On February 2016, the Ministry of Environment delivers to PDVSA the results of the analysis of the samples taken in the drainage channel of rainwater, located in the Los Caobos Urbanization, Araguaney Street, in addition to the samples taken in the deep well located in Los Caobos Urbanization, Av. 113. The laboratory results indicate that the canal is being reached by a mixture of water with a high concentration of total petroleum hydrocarbons (TPH), a product that can be gasoline in concentrations that are still a risk to health and the environment.

Regarding to the conclusion of the analysis of the samples taken in the deep well: the results indicate that the well is contaminated by total petroleum hydrocarbons (TPH) with a value of 22 mg / L and presents high concentrations of total iron (Fe) and total manganese (Mn) that is above the maximum ranges or limits

allowed in articles 5 and 8 of Decree 3219 for type 1 water unbundled Sub-Type 1A and 1B. Therefore, the waters are not suitable for human consumption.

Among May and August 2016, the Phase I of the environmental assessment was carried out in the Gas station El Prado with the GUEINPROCA Company. Between April and May 2017, the Geohidra Consultores Company was contracted by PDVSA Company, to develop the Project "Environmental Evaluation Phase II for the Determination of Levels of Pollution by Hydrocarbon Spilled in E / S El Prado, Carabobo State. The report presents the results obtained during the execution of the Phase II Environmental Assessment. The database used is taken from the records of the measurements, and the results of the physical and chemical analyzes of the soil and water samples.

#### **METHODS**

The database of this study has been obtained from two sources (Table 1); one is represented by Geohidra Consultores Company, which was contracted by the PDVSA Company between April and May 2017. The study can be accessed publicly from the headquarters of the Ministry of the Environment, Carabobo State. The second is a study developed by Rodriguez, (2017) to get the Science Master degree at the Environmental Engineering program of the University of Carabobo. In the first study, the activities that were developed during the phase II of the Environment Assessment implied: 1) Construction of monitoring wells: installation of monitoring wells with a diameter of two (2) inches, distributed in the potentially affected area according to the results of the Phase I of Environmental Evaluation. As a sample, the monitoring station 1 (PM-1) is located in the coordinates: N10°09'34" and W68°01'26.9" (Table 1). The depth of the drilled wells is between 7.3 m and 22.8 m, for a total of 166.86 m of drilling. 2)



Lithological study of the subsoil, taking samples every 1.5 meters of advance in the drilling. Physical tests in the laboratory that included: texture, liquid limit, plastic limit, plasticity index, moisture content, granulometry and permeability. Collection and analysis of soil samples: 15 soil samples were collected and analyzed. taking as a reference the concentration of Volatile Organic Compounds (VOC) in them. The following parameters were considered in the analysis: Total metals Methyl tertiary-butyl (Lead), (MTBE), Benzene, Toluene, Ethylenebenzene and Xylene (BTEX), Total Petroleum Hydrocarbons (TPH), TPH-GRO (GRO: Gasoline Range Organics,  $C_6$ - $C_{10}$ ), TPH-DRO (DRO: Diesel Range Organics, C<sub>10</sub>-C<sub>12</sub>, C<sub>12</sub>-C<sub>16</sub>) and TPH-ORO (ORO: Oil Range Organic, C<sub>16</sub>-C<sub>35</sub>). 4) Collection and analysis of water samples: 15 samples of groundwater were collected and analyzed, after cleaning the wells. The following parameters were considered in the analysis: Total metals Methyl tertiary-butyl (Lead), (MTBE), Benzene, Toluene, Ethylbenzene and Xylene (BTEX), Total Petroleum Hydrocarbons (TPH), **TPH-GRO** (Gasoline Range Organics, C<sub>6</sub>-C<sub>10</sub>), TPH-DRO (Diesel Range Organics, C<sub>10</sub>-C<sub>12</sub>, and TPH-ORO (ORO: Oil  $C_{12}$ - $C_{16}$ ), Range Organic, C<sub>16</sub>-C<sub>35</sub>). 5) Measurement of the depth of the water level in the monitoring wells constructed, and the thickness of the product or free hydrocarbon (if present).

The second study was carried out by the following activities: 1) Description of the topographic, geological, and hydrogeological characteristics of the La Guacamaya aquifer, Valencia Municipality, Carabobo State. Alos Palsar Satellite digital elevation model was acquired from webpage the https://vertex.daac.asf.alaska.edu/, and processed using the geographical information system software, ArcGIS

version 10.0. The lithological database was provided by the Ministry of Environment, Carabobo State. 2) Identification of the land uses in the La Guacamaya aquifer, Municipality of Valencia, Carabobo State. Landsat satellite image was processed using the ArcGIS software by classifying in three types of uses and covers: 1) urban, 2) vegetation, and 3) deforested soil. 3) Determination of the hydraulic parameters of the La Guacamaya aquifer, Valencia Carabobo Municipality, State. The Ministry of Environment provided information on static and dynamic levels; which combined with was measurements made in 7 pumping wells of water for human consumption industrial uses from the University of Carabobo using a mobile water level sensor for deep wells made by SEBA-Hydrometrie, 4) Estimation of physicochemical parameters groundwater sources. To obtain these data, water samples were collected in the 7 monitoring wells and processed by the Hidrolab Toro laboratory, determining the following physico-chemical parameters: Benzene, Toluene and o-Xylene. As a sample, the monitoring station 1 by the University of Carabobo (UC-1) is located in the coordinates: N10°09'18.6" and W68°01'53.6" (Table 1). 5) Simulation of the pollution plume for contaminants of the La Guacamaya aquifer. The results were obtained by applying of groundwater tool contained in the GIS software ArcGIS version 10.0.

In this study, three characteristics are presented with respect to the La Guacamaya aquifer: physical, 1) chemicals, 3) hydraulics. In the first, the physical characteristics are represented in maps (Figure 2 and Figure 3): 1) terrain elevation, 2) terrain slope, 3) geology, 4) geomorphology, 5) stream orders, 6) Land use / Land cover. In the second, the hydrocarbons combined database of measured in soil and water provided by



Geohidra, 2017 and Rodriguez, 2018 is used to adjust geostatistical models from deterministic methods based on global and local polynomial interpolation in order to make spatial distribution prediction of the hydrocarbons in La Guacamaya aquifer using the geostatistical analyst tool of ArcGIS v10.0 (Figure 4 to Figure 10). In the third, the hydraulic characteristics are represented in maps (Figure 11): 1) water static level, 2) dynamic level, 3) hydraulic

gradient, 4) saturated thickness, 5) flow velocity, and 6) flow discharge. Finally, a remediation proposal is included using the information on the three characteristics indicated before, equation of mass balance and equation linked to mass transfer process from liquid to gas media using the equation proposed by Sherwood and Holloway, (1940). These components are used to design a system of air injection and vapor extraction from soil.

Table: 1. Localization of monitoring wells in a Carabobo State aquifer, Venezuela

| N° | Identification | North      | West       | Elevation (masl) |
|----|----------------|------------|------------|------------------|
| 1  | PM-1           | 10 09 31.4 | 68 01 26.9 | 468.96           |
| 2  | PM-2           | 10 09 32.3 | 68 01 25.0 | 468.86           |
| 3  | PM-3           | 10 09 33.9 | 68 01 26.9 | 469.78           |
| 4  | PM-4           | 10 09 31.7 | 68 01 31.7 | 469.45           |
| 5  | PM-5           | 10 09 32.3 | 68 01 26.1 | 469.11           |
| 6  | PM-6           | 10 09 29.7 | 68 01 25.1 | 467.46           |
| 7  | PM-7           | 10 09 29.4 | 68 01 29.7 | 467.88           |
| 8  | PM-8           | 10 09 30.8 | 68 01 27.5 | 468.62           |
| 9  | PM-9           | 10 09 32.3 | 68 01 27.0 | 469.18           |
| 10 | PM-10          | 10 09 31.4 | 68 01 26.3 | 468.79           |
| 11 | PM-11          | 10 09 31.8 | 68 01 25.7 | 468.88           |
| 12 | PM-12          | 10 09 32.2 | 68 01 23.1 | 469.14           |
| 13 | PM-13          | 10 09 26.6 | 68 01 30.3 | 466.94           |
| 14 | PM-14          | 10 09 28.3 | 68 01 22.2 | 464.51           |
| 15 | PM-15          | 10 09 28.7 | 68 01 27.3 | 468.72           |
| 16 | UC-01          | 10 09 18.6 | 68 01 53.6 | 492              |
| 17 | UC-02          | 10 09 08.3 | 68 02 04.8 | 475              |
| 18 | UC-03          | 10 09 31.1 | 68 01 15.8 | 491              |
| 19 | UC-04          | 10 09 29.3 | 68 01 36.3 | 408              |
| 20 | UC-05          | 10 09 28.8 | 68 01 22.9 | 480              |
| 21 | UC-06          | 10 09 34.0 | 68 01 25.7 | 472              |
| 22 | UC-07          | 10 08 53.5 | 68 01 33.2 | 464              |

PM: monitoring well developed by Geohidra, (2017) for a study of Petroleum of Venezuela, S.A. (PDVSA), UC: monitoring wells operating for human consumption and industrial uses, which were measured by Rodriguez, (2018) for a study of Science Master of University of Carabobo.

#### **RESULTS**

The physical characteristics in a Carabobo State aquifer indicating monitoring wells are shown in Figure 2 and Table 2: a) Terrain Elevation (Figure 2a, Table 2) varies between 432 and 734 masl, most of the area of aquifer corresponding to 56% is

located in terrain surface elevations varying between 412 and 438 masl, the monitoring wells are located between 439 and 469 masl, b) Terrain slope (Figure 2b, Table 2) varies between 0 and 104%, most of the area of aquifer corresponding to 57% is located in terrain slope varying between 0 and 4.47%, the monitoring wells are located between 5 and 14%, c) Geology (Figure 2c. Table 2) constituted of two components: La Costa metamorphic suite (14.05%) and alluvial quaternary (85.94%), the monitoring wells are located in the alluvial quaternary, d) Geomorphology (Figure 2d, Table 2) are constituted of six components:



floodplain (15.27%), 2) alluvial plain (29.86%), 3) high plateau (43.12%), 4) stream valley (0.64%), 5) piedmont (9.58%) and 6) hill (1.50%). monitoring wells are located in the alluvial plain. The stream order (Figure 2e, Table 2) is classified in three levels according to the stream division. The streams of order 1 have a total length of 18275.06 m, the streams of order 2 of 7512.19 m, the streams of order 3 of 5912.72 m. The monitoring wells are located near of stream of order 1. The land cover and land use is classified in 1) vegetation (35.69%), 2) deforested soil (2.31%) and 3) urban (62.09%). The monitoring wells are located in the urban area. The lithological profiles shown in Figure 3 indicate that there are alternating layers of clay of low graded plasticity with well sand: corresponding to confined aquifer.

The statistics of chemical characteristics measured in soil samples extracted from 15 monitoring wells in a Carabobo State aquifer, Venezuela, are shown in Table 3, Figure 4, as sample the minimum and maximum values are extracted: a) Total Petroleum Hydrocarbons (TPH) varies between 40 and 6000 mg/kg, b) TPH GRO (C<sub>6</sub>-C<sub>10</sub>) (GRO: Gasoline Range Organics) varies between 0.005 and 142.6 mg/kg, TPH DRO (C<sub>10</sub>-C<sub>16</sub>) (DRO: Diesel Range Organics) varies between 0.5 and 18.8 mg/kg, TPH DRO (C<sub>16</sub>-C<sub>35</sub>) varies between 0.2 and 114.5 mg/kg, TPH ORO (ORO: Oil Range Organics) varies between 12.2 and 327.8 mg/kg, Lead (Pb) varies between 5 and 129 mg/kg, c) BTEX: B: Benzene varies between 0.005 and 1.23 mg/kg, T: Toluene varies between 0.005 and 2.07 mg/kg, E: Ethylbenzene varies between 0.2 and 1.09 mg/kg, and metha-Xylene varies between 0.005 and 2.614 mg/kg, ortho- Xylene varies between 0.005 and 0.97 mg/kg, MTBE: Methyl Tertiary-Butyl Ether varies

between 0.2 and 3.281 mg/kg. The box diagrams are overlapped indicating that there is not statistically significant difference between the set of values of TPH and congeners and Lead; likewise between BTEX and MTBE. There are atypical values, as a sample the value of 6000 mg/kg for the TPH measured in soil (Figure 4a). The atypical values vary between 2 and 4 times of values observed to 75% of total data set.

The statistics of chemical characteristics measured in water samples extracted from 15 monitoring wells in a Carabobo State aguifer, Venezuela, are shown in Table 4, Figure 5, as sample the minimum and maximum values are extracted: a) Total Petroleum Hydrocarbons (TPH) varies between 0.1 and 2.3 mg/l, b) TPH GRO  $(C_6-C_{10})$  varies between 0.005 and 679.14 mg/l, TPH DRO ( $C_{10}$ - $C_{16}$ ) varies between 0.1 and 2.2 mg/l, TPH DRO (C<sub>16</sub>-C<sub>35</sub>) varies between 0.1 and 6.4 mg/l, TPH ORO varies between 0.1 and 7.3 mg/l, Lead (Pb) is of 0.1 mg/l, c) BTEX: B: Benzene varies between 0.05 and 159223 µg/l, T: Toluene varies between 0.005 and 44850.0 µg/l, E: Ethylbenzene varies between 0.057 and 5130 µg/l, and metha-Xylene varies between 0.062 and 17800.0 µg/l, ortho- Xylene varies between 0.011 and 4830.0 µg/l, MTBE: Methyl Tertiary-Butyl Ether varies between 0.273 and 570593 µg/l. The box diagrams are overlapped indicating that there is not statistically significant difference between the set of values of TPH and congeners and Lead; likewise between BTEX and MTBE. There are atypical values, as a sample the value of 6000 mg/kg for the TPH measured in soil. There are atypical values, as a sample the value of 600 mg/l for the TPH GRO measured in water (Figure 5a). The atypical values vary between 2 and 4 times of values observed to 75% of total data set.



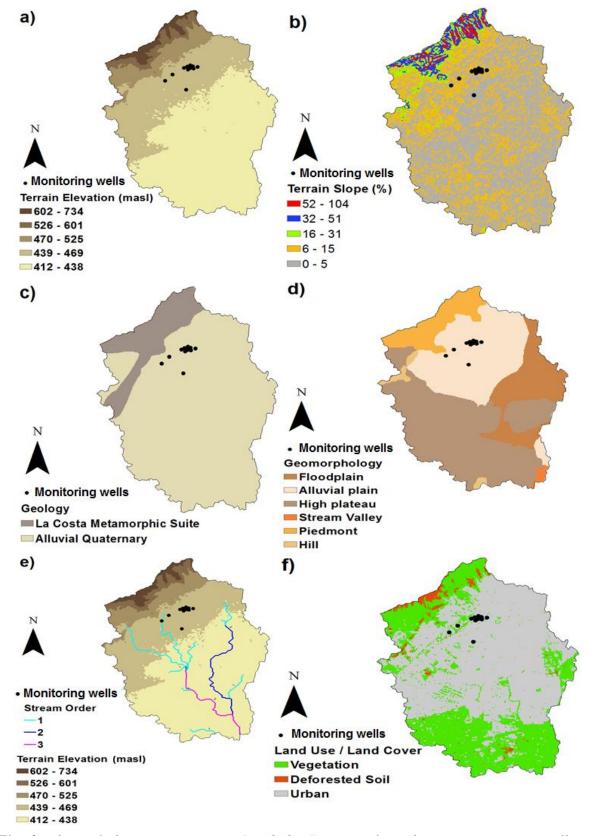


Fig: 2. Physical characteristics in a Carabobo State aquifer indicating monitoring wells: a) Terrain Elevation, b) Terrain slope, c) Geology, d) Geomorphology, e) Stream Order, f) Land Use/Land Cover



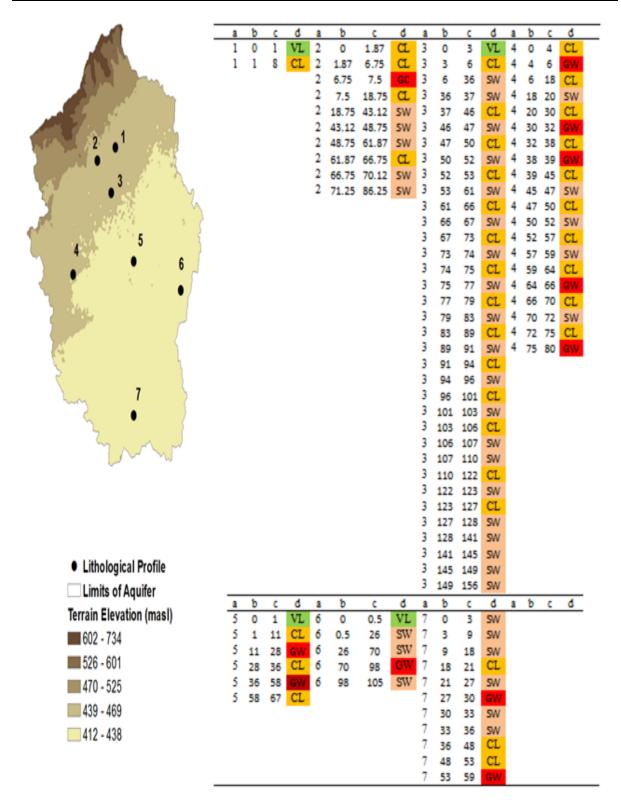
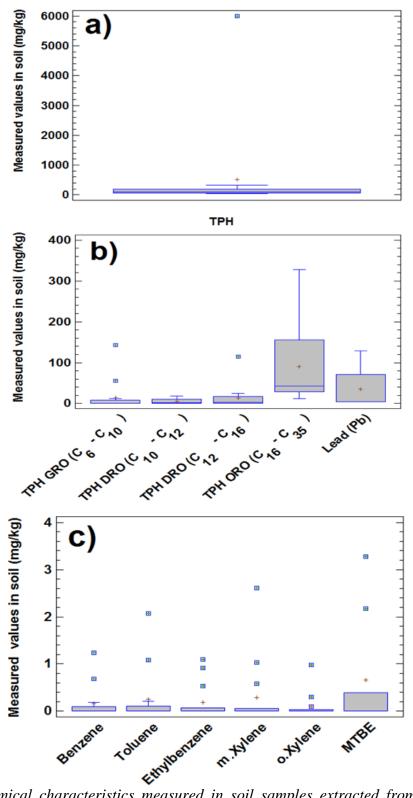


Fig: 3. Lithological profiles in a Carabobo State aquifer, Venezuela. a: number of lithological profile, b: upper limit of layer, c: lower limit of layer, d: soil type in the layer. The type of soil corresponds to the Unified Soil Classification System (USCS) as: GW: well-graded gravel, GC: clayey gravel, GM: silty gravel, SW: well-graded sand, SM: silty sand, SC: clayey sand, CL: clay of low plasticity, ML: silt, VL: vegetation layer, R: Rock.





**Fig: 4.** Chemical characteristics measured in soil samples extracted from 15 monitoring wells in a Carabobo State aquifer, Venezuela: a) Total Petroleum Hydrocarbons (TPH), b) TPH GRO ( $C_6$ - $C_{10}$ ) (GRO: Gasoline Range Organics), TPH DRO ( $C_{10}$ - $C_{16}$ ) (DRO: Diesel Range Organics), TPH DRO ( $C_{16}$ - $C_{35}$ ), TPH ORO (ORO: Oil Range Organics), Lead (Pb), c) BTEX: B: Benzene, T: Toluene, E: Ethylbenzene and X: Xylene (metha-Xylene, ortho-Xylene), MTBE: Methyl Tertiary-Butyl Ether



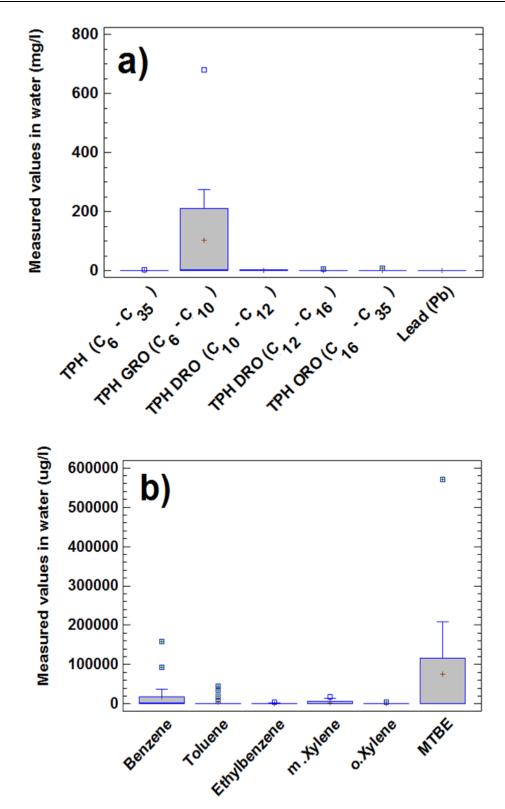


Fig: 5. Chemical characteristics measured in water samples extracted from 15 monitoring wells in a Carabobo State aquifer, Venezuela: a) Total Petroleum Hydrocarbons (TPH), b) TPH GRO ( $C_6$ - $C_{10}$ ) (GRO: Gasoline Range Organics), TPH DRO ( $C_{10}$ - $C_{16}$ ) (DRO: Diesel Range Organics), TPH DRO ( $C_{16}$ - $C_{35}$ ), TPH ORO (ORO: Oil Range Organics), Lead (Pb)



**Table: 2.** Physical characteristics in a Carabobo State aquifer indicating monitoring wells: a) Terrain Elevation, b) Terrain slope, c) Geology, d) Geomorphology, e) Stream Order, f) Land Use/Land Cover

| Unit N°     | Minimum       | Maximum  | Area (m²)        | Percentage of area | Length(m) |
|-------------|---------------|----------|------------------|--------------------|-----------|
| Terrain ele | vation (masl) |          |                  |                    |           |
| 1           | 412           | 438      | 30724530         | 56.17              |           |
| 2           | 439           | 469      | 15811560         | 28.90              |           |
| 3           | 470           | 525      | 4451406          | 8.14               |           |
| 4           | 526           | 601      | 2144531          | 3.92               |           |
| 5           | 602           | 734      | 1571563          | 2.87               |           |
|             |               |          | Terrain slope (  | %)                 |           |
| 1           | 0             | 4.472136 | 31531410         | 57.64              |           |
| 2           | 5.09902       | 14.56022 | 17988750         | 32.88              |           |
| 3           | 14.76482      | 31.01612 | 2519219          | 4.61               |           |
| 4           | 31.04835      | 50.59644 | 1849531          | 3.38               |           |
| 5           | 50.63596      | 104.0865 | 814687.5         | 1.49               |           |
|             |               |          | Geology          |                    |           |
| 1           |               |          | 621472500        | 14.05              |           |
| 2           |               |          | 3799290000       | 85.94              |           |
|             |               |          | Geomorpholog     | gy                 |           |
| 1           |               |          | 675345000        | 15.27              |           |
| 2           |               |          | 1320247500       | 29.86              |           |
| 3           |               |          | 1906245000       | 43.12              |           |
| 4           |               |          | 28545000         | 0.64               |           |
| 5           |               |          | 423637500        | 9.58               |           |
| 6           |               |          | 66742500         | 1.50               |           |
|             |               |          | Stream Orde      | r                  |           |
| 1           |               |          |                  |                    | 18275.06  |
| 2           |               |          |                  |                    | 7512.19   |
| 3           |               |          |                  |                    | 5912.72   |
|             |               |          | Land use /Land o | over               |           |
| 1           |               |          | 19478700         | 35.59              |           |
| 2           |               |          | 1266300          | 2.31               |           |
| 3           |               |          | 33984000         | 62.09              |           |

**Table: 3.** Statistics of chemical characteristics measured in soil samples extracted from 15 monitoring wells in a Carabobo State aquifer, Venezuela: a) Total Petroleum Hydrocarbons (TPH), b) TPH GRO ( $C_6$ - $C_{10}$ ) (GRO: Gasoline Range Organics), TPH DRO ( $C_{10}$ - $C_{16}$ ) (DRO: Diesel Range Organics), TPH DRO ( $C_{16}$ - $C_{35}$ ), TPH ORO (ORO: Oil Range Organics), Lead (Pb), c) BTEX: B: Benzene, T: Toluene, E: Ethylbenzene and X: Xylene (metha-Xylene, ortho-Xylene), MTBE: Methyl Tertiary-Butyl Ether

|   | Unit  | Count | Average  | Standard deviation | Coeff. of variation | Minimum | Maximum |
|---|-------|-------|----------|--------------------|---------------------|---------|---------|
| ТРН   | mg/kg | 15    | 509.707  | 1521.13            | 298.432%            | 40.0    | 6000.0  |
| TPH GRO (C <sub>6</sub> -C <sub>10</sub> )  | mg/kg | 15    | 15.2552  | 38.0223            | 249.241%            | 0.005   | 142.6   |
| TPH DRO (C <sub>10</sub> -C <sub>12</sub> ) | mg/kg | 15    | 5.16667  | 6.57459            | 127.25%             | 0.5     | 18.8    |
| TPH DRO (C <sub>12</sub> -C <sub>16</sub> ) | mg/kg | 15    | 13.6733  | 28.9309            | 211.586%            | 0.2     | 114.5   |
| TPH ORO (C <sub>16</sub> -C <sub>35</sub> ) | mg/kg | 15    | 90.3067  | 88.4461            | 97.9397%            | 12.2    | 327.8   |
| Lead (Pb)                                   | mg/kg | 15    | 34.8667  | 40.951             | 117.45%             | 5.0     | 129.0   |
| Benzene                                     | mg/kg | 15    | 0.158333 | 0.345033           | 217.915%            | 0.005   | 1.234   |
| Toluene                                     | mg/kg | 15    | 0.2436   | 0.574957           | 236.025%            | 0.005   | 2.072   |
| Ethylbenzene                                | mg/kg | 15    | 0.182333 | 0.361731           | 198.39%             | 0.005   | 1.097   |
| m.Xylene                                    | mg/kg | 15    | 0.289667 | 0.706394           | 243.864%            | 0.005   | 2.614   |
| o.Xylene                                    | mg/kg | 15    | 0.0974   | 0.25546            | 262.279%            | 0.005   | 0.978   |
| MTBE  | mg/kg | 15    | 0.660633 | 1.19642            | 181.102%            | 0.005   | 3.281   |



**Table: 4.** Statistics of chemical characteristics measured in water samples extracted from 15 monitoring wells in a Carabobo State aquifer, Venezuela: a) Total Petroleum Hydrocarbons (TPH), b) TPH GRO ( $C_6$ - $C_{10}$ ) (GRO: Gasoline Range Organics), TPH DRO ( $C_{10}$ - $C_{16}$ ) (DRO: Diesel Range Organics), TPH DRO ( $C_{16}$ - $C_{35}$ ), TPH ORO (ORO: Oil Range Organics), Lead (Pb), c) BTEX: B: Benzene, T: Toluene, E: Ethylbenzene and X: Xylene (metha-Xylene, ortho-Xylene), MTBE: Methyl Tertiary-Butyl Ether

|  | Unit | Count | Average  | Standard  | Coeff. of variation | Minimum | Maximum |
|--|------|-------|----------|-----------|---------------------|---------|---------|
|  |      |       |          | deviation |                     |         |         |
| TPH (C <sub>6</sub> - C <sub>35</sub> )      | mg/l | 15    | 0.506667 | 0.568792  | 112.261%            | 0.1     | 2.3     |
| TPH GRO (C $_6$ - C $_{10}$ )                | mg/l | 15    | 103.035  | 189.753   | 184.164%            | 0.005   | 679.14  |
| TPH DRO (C 10 - C 12)                        | mg/l | 15    | 0.72     | 0.824794  | 114.555%            | 0.1     | 2.2     |
| TPH DRO ( $C_{12}$ - $C_{16}$ )              | mg/l | 15    | 0.66     | 1.60704   | 243.491%            | 0.1     | 6.4     |
| TPH ORO (C <sub>16</sub> - C <sub>35</sub> ) | mg/l | 15    | 0.773333 | 1.81402   | 234.571%            | 0.1     | 7.3     |
| Lead (Pb)                                    | mg/l | 15    | 0.1      | 0         | 0%                  | 0.1     | 0.1     |
| Benzene                                      | μg/l | 22    | 18127.3  | 37977.2   | 209.502%            | 0.05    | 159223. |
| Toluene                                      | μg/l | 22    | 4987.13  | 12304.7   | 246.729%            | 0.05    | 44850.0 |
| Ethylbenzene                                 | μg/l | 15    | 736.948  | 1407.42   | 190.98%             | 0.057   | 5130.0  |
| m.Xylene                                     | μg/l | 15    | 3148.91  | 5637.32   | 179.024%            | 0.062   | 17800.0 |
| o.Xylene                                     | μg/l | 19    | 805.805  | 1649.16   | 204.66%             | 0.011   | 4830.0  |
| MTBE   | μg/l | 15    | 76111.3  | 153631.   | 201.85%             | 0.273   | 570593. |

spatial prediction of chemical characteristics measured in soil samples extracted from 15 monitoring wells in a Carabobo State aquifer, Venezuela, are shown in Figure 6 and Table 5: a) Total Petroleum Hydrocarbons (TPH): source of maximum contamination is close to the monitoring stations PM-4, PM-9 and PM-12. This spatial prediction is explained by a local polynomial interpolation with order 3, Kernell function of Epanechnikov and a gradient of linear regression function of 0.28 b) TPH GRO ( $C_6$ - $C_{10}$ ) the source of maximum contamination is close to the monitoring stations PM-4, and PM-7. This spatial prediction is explained by a local polynomial interpolation with order 3, Kernell function of Quartic and a gradient of linear regression function of 0.59, c) DRO  $(C_{10}$ - $C_{16})$  the source of maximum contamination is close to the monitoring stations PM-4, and PM-7. This spatial prediction is explained by a local polynomial interpolation with order 2, Kernell function of Polynomial order 5 and a gradient of linear regression function of 0.67, d) TPH DRO ( $C_{16}$ - $C_{35}$ ) the source of maximum contamination is close to the monitoring stations PM-4, and PM-9. This spatial prediction is explained by a local polynomial interpolation with order 3, Kernell function of Exponential and a gradient of linear regression function of 0.80, e) TPH ORO the source of maximum contamination is close to the monitoring stations PM-4, and PM-12. This spatial prediction is explained by a local polynomial interpolation with order 3, Kernell function of Gaussian and a gradient of linear regression function of 0.80, f) Lead (Pb) the source of maximum contamination is close to the monitoring stations PM-4, PM-3 and PM-12. This spatial prediction is explained by a local polynomial interpolation with order 2, Kernell function of Epanechinov and a gradient of linear regression function of 0.94. The spatial prediction of chemical characteristics measured in soil samples extracted from 15 monitoring wells in a Carabobo State aguifer, Venezuela, are shown in Figure 7 and Table 5: BTEX: a) the source of maximum Benzene: contamination is close to the monitoring stations PM-6, PM13 and PM-15. This spatial prediction is explained by a local polynomial interpolation with order 3, Kernell function of Exponential and a gradient of linear regression function of 0.72, b) Toluene the source of maximum contamination is close to the monitoring stations PM-6, and PM-15. This spatial prediction is explained by a global polynomial interpolation with order 3 and



a gradient of linear regression function of 0.94, *c) Ethylbenzene* the source of maximum contamination is close to the monitoring stations PM-6, PM-13, and PM-15, *d) metha-Xylene* the source of maximum contamination is close to the monitoring stations PM-6, PM-13 and PM-15. This spatial prediction is explained by a global polynomial interpolation with order 3 and a gradient of linear regression function of 0.93, *e) ortho- Xylene* the source of maximum contamination is close to the monitoring stations PM-6, PM13

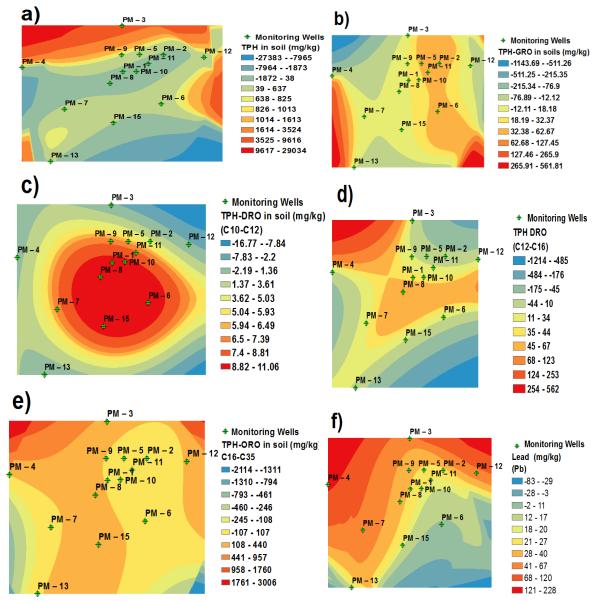
and PM-15. This spatial prediction is local explained by a polynomial interpolation with order 3, Kernell function of Gaussian and a gradient of linear regression function of 0.72, f) MTBE: Methyl Tertiary-Butyl Ether the source of maximum contamination is close to the monitoring stations PM-6, PM13 and PM-15. This spatial prediction is explained by a global polynomial interpolation with order 2 and a gradient of linear regression function of 0.

**Table: 5.** Statistics of spatial prediction using deterministic methods of chemical characteristics measured in soil samples extracted from 15 monitoring wells in a Carabobo State aquifer, Venezuela: a) Total Petroleum Hydrocarbons (TPH), b) TPH GRO ( $C_6$ - $C_{10}$ ) (GRO: Gasoline Range Organics), c)TPH DRO ( $C_{10}$ - $C_{16}$ ) (DRO: Diesel Range Organics), d) TPH DRO ( $C_{16}$ - $C_{35}$ ), e) TPH ORO (ORO: Oil Range Organics), f) Lead (Pb)

| Physico-Chemical Parameters | Unit   | SSPM      | Ordinary Krigging                         |
|-----------------------------|--------|-----------|---|
| TPH                         | mg/kg  | DM        | Local polynomial Interpolation            |
|                             |        | OP        | 3   |
|                             |        | KF        | Epanechnikov                              |
|                             |        | PRF       | 0.28460520671002 * x + -1985.67972779922  |
| TPH GRO                     | mg/kg  | DM        | Local polynomial Interpolation            |
| $(C_6-C_{10})$              |        | OP        | 3   |
|                             |        | KF        | Quartic                                   |
|                             |        | PRF       | 0.592769642106749 * x + -87.7323506810128 |
| TPH DRO                     | mg/kg  | DM        | Local polynomial Interpolation            |
| $(C_{10}-C_{12})$           |        | OP        | 2   |
|                             |        | KF        | Polynomial order 5                        |
|                             |        | PRF       | 0.671841146677751 * x + -1.76870993567521 |
| TPH DRO                     | mg/kg  | DM        | Local polynomial Interpolation            |
| $(C_{12}-C_{16})$           |        | OP        | 3   |
|                             |        | KF        | Exponential                               |
|                             |        | PRF       | 0.804922181333584 * x + -26.8747504061333 |
| TPH ORO                     | mg/kg  | DM        | Local polynomial Interpolation            |
| $(C_{16}-C_{35})$           |        | OP        | 3   |
|                             |        | KF        | Gaussian                                  |
| T 1                         |        | PRF<br>DM | 0.804922181333584 * x + -26.8747504061333 |
| Lead                        | mg/kg  |           | Local polynomial Interpolation 2          |
|                             |        | OP<br>KF  | Epanechnikov                              |
|                             |        | PRF       | 0.94409190209168 * x + 5.35687906663836   |
| Benzene                     | mg/kg  | DM        | Local polynomial Interpolation            |
| Denzene                     | mg/kg  | OP        | 2   |
|                             |        | KF        | Exponential                               |
|                             |        | PRF       | 0.720555712 * x + -1.1334187876           |
| Toluene                     | mg/kg  | DM        | Global polynomial Interpolation           |
| Totache                     | mg/ Ng | OP        | 3   |
|                             |        | PRF       | 0.938500937909668 * x + -1.44489029786802 |
| m.Xyelene                   | mg/kg  | DM        | Global polynomial Interpolation           |
| ,                           | 88     | OP        | 3   |
|                             |        | PRF       | 0.938500937909668 * x + -1.44489029786802 |
| o.Xyelene                   | mg/kg  | DM        | Local polynomial Interpolation            |
| , and a                     | 8 8    | OP        | 3   |
|                             |        | KF        | Gaussian                                  |
|                             |        | PRF       | 1.12097503729533 * x + -0.456425358301639 |
| MTBE                        | mg/kg  | DM        | Global polynomial Interpolation           |
|                             | 0 0    | OP        | 2   |
|                             |        | PRF       | 0.348548847562566 * x + 0.29913467178114  |

OP: Order of polynomial, KF: Kernel Function, PRF: Predicted Regression Function





**Fig: 6.** Spatial prediction of chemical characteristics measured in soil samples extracted from 15 monitoring wells in a Carabobo State aquifer, Venezuela: a) Total Petroleum Hydrocarbons (TPH), b) TPH GRO ( $C_6$ - $C_{10}$ ) (GRO: Gasoline Range Organics), c)TPH DRO ( $C_{10}$ - $C_{16}$ ) (DRO: Diesel Range Organics), d) TPH DRO ( $C_{16}$ - $C_{35}$ ), e) TPH ORO (ORO: Oil Range Organics), f) Lead (Pb)



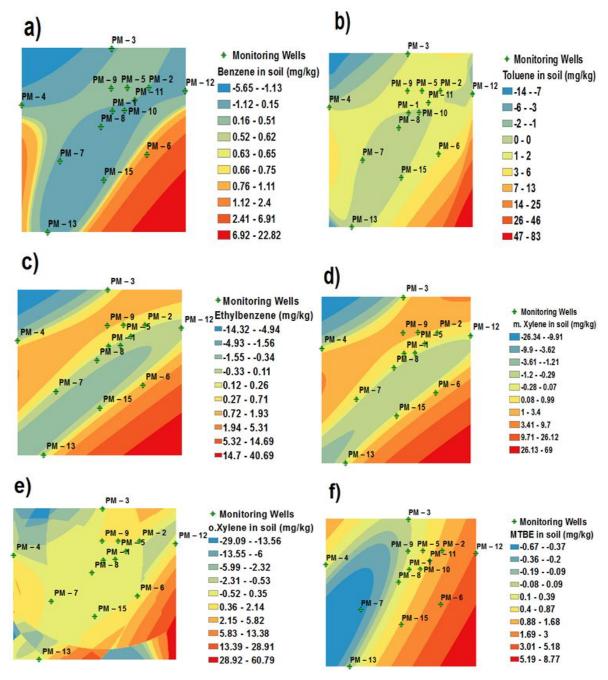


Fig: 7. Spatial prediction of chemical characteristics measured in soil samples extracted from 15 monitoring wells in a Carabobo State aquifer, Venezuela: BTEX: a) Benzene, b) Toluene, c) Ethylbenzene d) metha-Xylene, e) ortho- Xylene, f) MTBE: Methyl Tertiary-Butyl Ether

The spatial prediction of chemical characteristics measured in water samples extracted from 15 monitoring wells in a Carabobo State aquifer, Venezuela, are shown in Figure 8 and Table 6: *a) TPH* the source of maximum contamination is close to the monitoring stations PM-4,

PM-6, PM-12 PM-15. This spatial prediction is explained by a local polynomial interpolation with order 3, Kernell function of Quartic order and a gradient of linear regression function of 0.39, *b*) *TPH GRO* ( $C_6$ - $C_{10}$ ) the source of maximum contamination is close to the



monitoring stations PM-2, PM-7 and PM-15. This spatial prediction is explained by a local polynomial interpolation with order 2, Kernell function of Polynomial 5 order and a gradient of linear regression function of 0.56, c) TPH DRO ( $C_{10}$ - $C_{16}$ ) the source of maximum contamination is close to the monitoring stations PM-2, PM-7 and PM-15. This spatial prediction is explained by a local polynomial interpolation with order 2, Kernell function of Polynomial 5 order and a gradient of linear regression function of 0.57, d) TPH DRO ( $C_{16}$ - $C_{35}$ ) the source of maximum contamination is close to the monitoring stations PM-2, PM-7 and PM-15. This spatial prediction is explained by a local polynomial interpolation with order 3, Kernell function of Exponential and a gradient of linear regression function of 0.55, e) TPH ORO the source of maximum contamination is close to the monitoring stations PM-2, PM-7 and PM-15. This spatial prediction is explained by a local polynomial interpolation with order 2, Kernell function of Exponential and a gradient of linear regression function of 0.27.

prediction of The spatial chemical characteristics measured in water samples extracted from 15 monitoring wells in a Carabobo State aquifer, Venezuela, are shown in Figure 9 and Table 6: BTEX: a) the maximum Benzene: source of contamination is close to the monitoring stations PM-7, PM12 and PM-15. This spatial prediction is explained by a local polynomial interpolation with order 2, Kernell function of Polynomial 5 order and a gradient of linear regression function of 0.55, b) Toluene the source of maximum contamination is close to the monitoring stations PM-7, PM12 and PM-15. This spatial prediction is explained by a global polynomial interpolation with order 2 and a gradient of linear regression function of 0.41, c) Ethylbenzene the source of maximum contamination is close to the monitoring stations PM-7, PM12 and PM-

15. d) metha-Xylene the source of maximum contamination is close to the monitoring stations PM-7, PM12 and PM-15. This spatial prediction is explained by a global polynomial interpolation with order 3 and a gradient of linear regression function of 1.44, e) ortho- Xylene the source of maximum contamination is close to the monitoring stations PM-7, PM12 and PM-15. This spatial prediction is polynomial explained by a local interpolation with order 2, Kernell function of Epanechnikov and a gradient of linear regression function of 0.41, f) MTBE: Methyl Tertiary-Butyl Ether the source of maximum contamination is close to the monitoring stations PM-7, PM12 and PM-15. This spatial prediction is explained by a local polynomial interpolation with order 2, Kernell function of Epanechnikov and a gradient of linear regression function of 0.62.

The statistics of spatial prediction of chemical characteristics measured in water samples extracted from 15 monitoring wells developed by PDVSA (Petroleos de Venezuela, S.A.) combined with the water samples extracted from 7 monitoring wells for domestic and industrial uses by the University of Carabobo in a Carabobo State aquifer, Venezuela, are shown in Figure 10 and Table 7: BTEX: a) Benzene the source of maximum contamination is close to the monitoring stations PM-1 to PM-15. This spatial prediction is explained by a local polynomial interpolation with order 2, Kernell function of Exponential and a gradient of linear regression function of 0.94, b) Toluene the source of maximum contamination is close to the monitoring stations PM-1 to PM-15. This spatial prediction is explained by a local polynomial interpolation with order 2, Kernell function of Exponential and a gradient of linear regression function of 0.94, c) ortho- Xylene the source of maximum contamination is close to the monitoring stations PM-1 to PM-15. This



spatial prediction is explained by a local polynomial interpolation with order 2, Kernell function of Exponential and a gradient of linear regression function of 0.72.

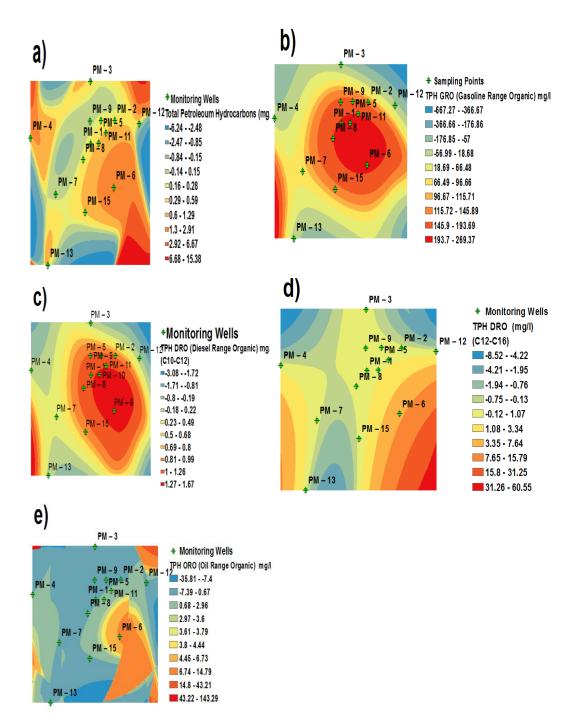


Fig: 8. Spatial prediction of chemical characteristics measured in water samples extracted from 15 monitoring wells in a Carabobo State aquifer, Venezuela: a) Total Petroleum Hydrocarbons (TPH), b) TPH GRO ( $C_6$ - $C_{10}$ ) (GRO: Gasoline Range Organics), c)TPH DRO ( $C_{10}$ - $C_{16}$ ) (DRO: Diesel Range Organics), d) TPH DRO ( $C_{16}$ - $C_{35}$ ), e) TPH ORO (ORO: Oil Range Organics)



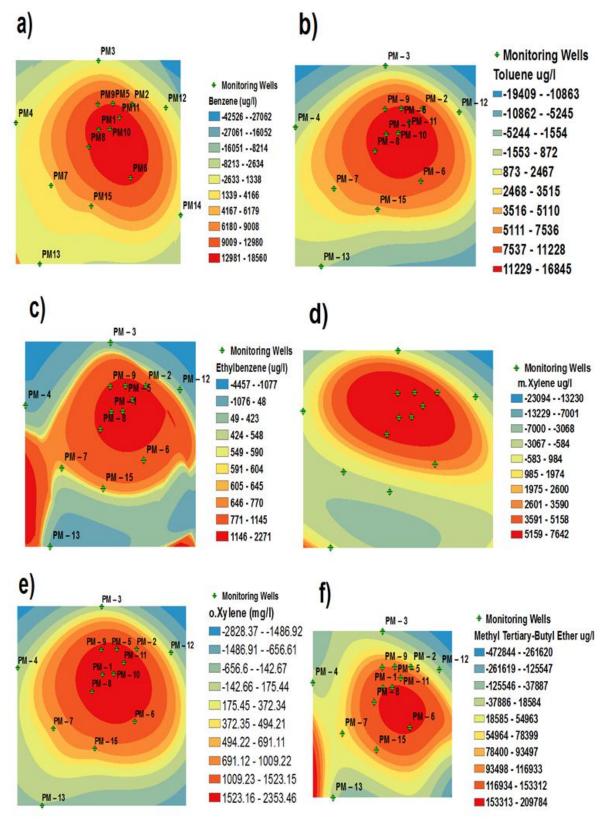


Fig: 9. Spatial prediction of chemical characteristics measured in water samples extracted from 15 monitoring wells in a Carabobo State aquifer, Venezuela: BTEX: a) Benzene, b) Toluene, c) Ethylbenzene, d) metha-Xylene, e) ortho- Xylene, f) MTBE: Methyl Tertiary-Butyl Ether



**Table: 6.** Statistics of spatial prediction using deterministic methods of chemical characteristics measured in water samples extracted from 15 monitoring wells in a Carabobo State aquifer, Venezuela: a) Total Petroleum Hydrocarbons (TPH), b) TPH GRO ( $C_6$ - $C_{10}$ ) (GRO: Gasoline Range Organics), c)TPH DRO ( $C_{10}$ - $C_{16}$ ) (DRO: Diesel Range Organics), d) TPH DRO ( $C_{16}$ - $C_{35}$ ), e) TPH ORO (ORO: Oil Range Organics), f) Lead (Pb)

| Physico-Chemical<br>Parameters              | Unit | SSPM     | Ordinary Krigging                                     |
|---|------|----------|---|
| ТРН   | mg/l | DM       | Local polynomial Interpolation                        |
| 1111  | mg/1 | OP       | 3   |
|   |      | KF       | Ouartic   |
|   |      | PRF      | 0.393873326501493 * x + 1.41654438124167              |
| TPH GRO                                     | mg/l | DM       | Local polynomial Interpolation                        |
| $(C_6-C_{10})$                              | 8    | OP       | 2   |
|   |      | KF       | Polynomial 5 order                                    |
|   |      | PRF      | 0.562194612940361 * x + -83.961325297697              |
| TPH DRO (C <sub>10</sub> -C <sub>12</sub> ) | mg/l | DM       | Local polynomial Interpolation                        |
|   |      | OP       | 2   |
|   |      | KF       | Polynomial 5 order                                    |
|   |      | PRF      | 0.577097044129682 * x + 0.0695809554385322            |
| <b>TPH DRO</b> $(C_{12}$ <b>-</b> $C_{16})$ | mg/l | DM       | Local polynomial Interpolation                        |
|   |      | OP       | 3   |
|   |      | KF       | Exponential   |
|   |      | PRF      | 0.556762849317677 * x + -1.3256336761485              |
| TPH ORO                                     | mg/l | DM       | Local polynomial Interpolation                        |
| $(C_{16}-C_{35})$                           |      | OP       | 3   |
|   |      | KF       | Exponential   |
|   |      | PRF      | 0.270640968049954 * x + -1.86469971122671             |
| Benzene                                     | mg/l | DM       | Local polynomial Interpolation                        |
|   |      | OP       | 2   |
|   |      | KF       | Polynomial 5 order                                    |
|   | _    | PRF      | 0.557038097965685 * x + -2027.5095566665              |
| Toluene                                     | mg/l | DM       | Local polynomial Interpolation                        |
|   |      | OP<br>KF |   |
|   |      | PRF      | Exponential 0.408504049756411 * x + -3666.53299941957 |
| m.Xyelene                                   | mg/l | DM       | Global polynomial Interpolation                       |
| m.zyciene                                   | mg/1 | OP       | 3   |
|   |      | PRF      | 1.44440406488439 * x + -12450.0031999271              |
| o.Xyelene                                   | mg/l | DM       | Local polynomial Interpolation                        |
|   |      | OP       | 2   |
|   |      | KF       | Epanechnikov  |
|   |      | PRF      | 0.408504049756411 * x + -3666.53299941957             |
| MTBE  | mg/l | DM       | Local polynomial Interpolation                        |
|   | Ü    | OP       | 2   |
|   |      | KF       | Epanechnikov  |
|   |      | PRF      | 0.682614467587869 * x + -1203.50323913832             |

OP: Order of polynomial, KF: Kernel Function, PRF: Predicted Regression Function



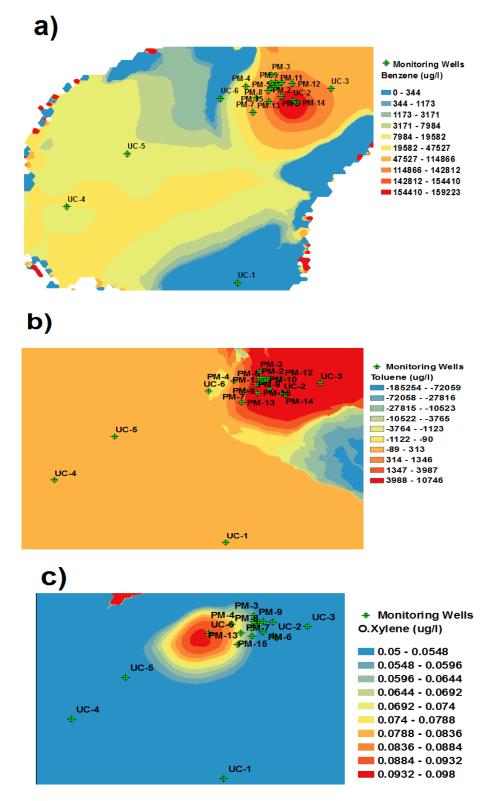


Fig: 10. Spatial prediction of chemical characteristics measured in water samples extracted from 15 monitoring wells developed by PDVSA (Petroleos de Venezuela, S.A.) combined with the water samples extracted from 7 monitoring wells for domestic and industrial uses by the University of Carabobo in a Carabobo State aquifer, Venezuela: BTEX: a) Benzene, b) Toluene, c) Ethylbenzene



**Table:** 7. Statistics of spatial prediction of chemical characteristics measured in water samples extracted from 15 monitoring wells developed by PDVSA (Petroleos de Venezuela, S.A.) combined with the water samples extracted from 7 monitoring wells for domestic and industrial uses by the University of Carabobo in a Carabobo State aquifer, Venezuela: BTEX: a) Benzene, b) Toluene, c) ortho- Xylene

| Physico-          | Unit | SSPM | Ordinary Krigging                          |
|-------------------|------|------|--|
| Chemical          |      |      |  |
| <b>Parameters</b> |      |      |  |
| Benzene           | mg/l | DM   | Local polynomial Interpolation             |
|                   |      | OP   | 2  |
|                   |      | KF   | Exponential                                |
|                   |      | PRF  | 0.948897164056249 * x + 986.718386069828   |
| Toluene           | mg/l | DM   | Local polynomial Interpolation             |
|                   |      | OP   | 2  |
|                   |      | KF   | Exponential                                |
|                   |      | PRF  | 0.941560191957777 * x + 11.5130611412567   |
| o. Xylene         | mg/l | DM   | Local polynomial Interpolation             |
| •                 | _    | OP   | 2  |
|                   |      | KF   | Exponential                                |
|                   |      | PRF  | 0.723500847430219 * x + 0.0143122609235567 |

OP: Order of polynomial, KF: Kernel Function, PRF: Predicted Regression Function

Hydraulic parameters in a Carabobo State aguifer, Venezuela, are shown in Figure a) Water static level, b) Water dynamic level, c) Hydraulic gradient, d) Saturated Thickness, e) Flow Velocity, f) Flow discharge: a) Water static level (Figure 11a, Table 8) varies between 407.62 and 686.10 masl, most of the area of aquifer corresponding to 57% is located in water static level varying between 407 and 433 masl, b) Water dynamic level (Figure 11b, Table 8) varies between 358.09 and 663.68 masl, most of the area of aquifer corresponding to 61.36% is located in Water dynamic levels varying between 358.09 and 663.78 masl, c) Hydraulic gradient (Figure 11c, Table 8) varies between 0.01 and 62.43 %, most of the area of aquifer corresponding to 68.17% is located in hydraulic gradient varying between 0.01 and 3.25%, d) Saturated Thickness, (Figure 11d, Table 8) varies between 35 and 99 m, most of the area of aquifer corresponding to 39.96% is located in saturated thickness varying between 45 and 54 m, e) Flow velocity, (Figure 11e, Table 8) varies between 0.03 and 84.14 m/d, most of the area of aquifer corresponding to 68.75% is located in flow

velocity varying between 2.25 and 68.75 m/d, f) Flow discharge, (Figure 11f, Table 8) varies between 330 and 841405 m<sup>3</sup>/d, most of the area of aquifer corresponding to 68.75% is located in flow discharge varying between 330 and 46339 m<sup>3</sup>/d.

The mass flow in a Carabobo State aquifer, Venezuela, is shown in Figure 12: *BTEX: a) Benzene:* the maximum mass flow is 15837.1 kg/d, *b) Toluene:* the maximum mass flow is 557.31 kg/d, c) ortho- Xylene: the maximum mass flow is 0.156 kg/d.

The parameters for remediation applying air injection and vapor extraction in a Carabobo State aquifer, Venezuela, are shown in Table 9: *For Benzene:* the required air is 13153 m³/d (323 cfm) and the vapor extraction is 5075 m³/d (125 cfm). *For Toluene:* the required air is 463 m³/d (11.35 cfm) and the vapor extraction is 6.28 m³/d (3.7 cfm). *For O-Xylene:* the required air is 0.13 m³/d (0.014 cfm) and the vapor extraction is 0.036 m³/d (0.000882 cfm). The proposed wells for air injection (42) and vapor extraction (19) in a Carabobo State aquifer polluted with



Benzene separated each 100 meters and 150 meters, respectively are shown in Figure 13. The regulatory limit for the Benzene in water is 10  $\mu$ g/l according to the Sanitary Standard for Drinking Water

Quality, Official Gazette Venezuela. N° 36395 Art. 14. The distribution of wells is valid for treatment of the rest of hydrocarbons referenced in Figures 8 and 9.

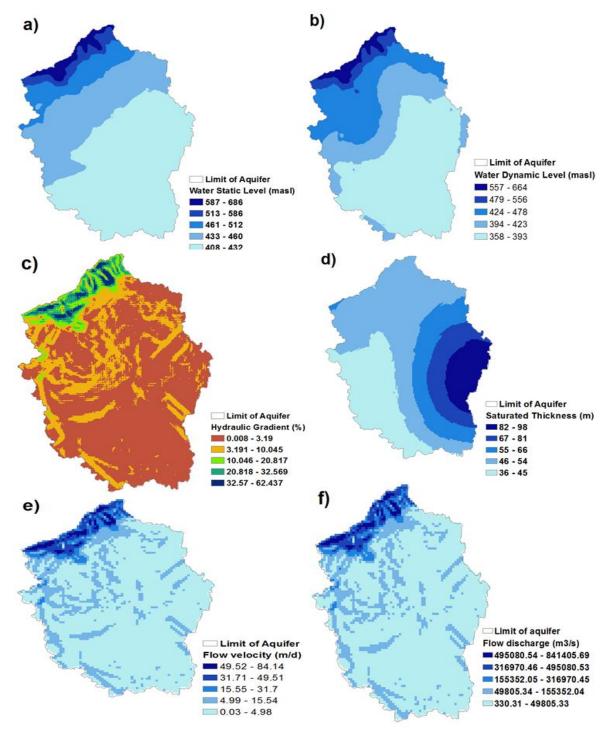


Fig: 11. Hydraulic parameters in a Carabobo State aquifer, Venezuela: a) Water static level, b) Water dynamic level, c) Hydraulic gradient, d) Saturated Thickness, e) Flow Velocity, f) Flow discharge



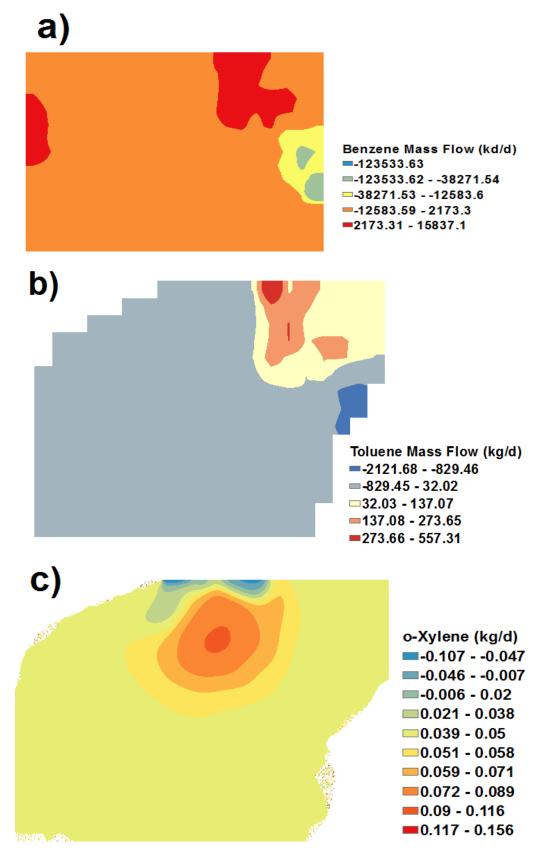


Fig: 12. Mass Flow in a Carabobo State aquifer, Venezuela: BTEX: a) Benzene, b) Toluene, c) Ethylbenzene



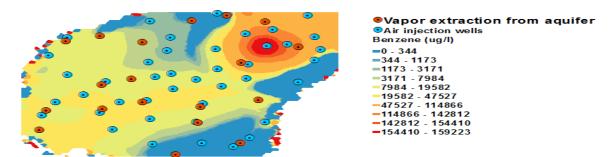


Fig: 13. Proposed wells for air injection (42) and vapor extraction (19) in a Carabobo State aquifer polluted with Benzene separated each 100 meters and 150 meters, respectively. The regulatory limit for the Benzene in water is 10  $\mu$ g/l according to the Sanitary Standard for Drinking Water Quality, Official Gazette Venezuela. N° 36395 Art. 14.

**Table:** 8. Statistics for hydraulic parameters in a Carabobo State aquifer, Venezuela: a) Water static level, b) Water dynamic level, c) Hydraulic Gradient, d) Saturated Thickness, e) Flow velocity, f) Flow transmissivity

| Unit N°      | Minimum                  | Maximum  | Area (m <sup>2</sup> ) | Percentage of area |
|--------------|--------------------------|----------|------------------------|--------------------|
| Water statio | c level (masl)           |          |                        |                    |
| 1            | 407.62                   | 433.00   | 30596400               | 55.94              |
| 2            | 433.01                   | 460.81   | 15021150               | 27.46              |
| 3            | 460.82                   | 512.64   | 5155405                | 9.42               |
| 4            | 512.77                   | 585.51   | 2149985                | 3.93               |
| 5            | 585.59                   | 686.10   | 1767369                | 3.23               |
| Water dyna   | amic level (masl)        |          |                        |                    |
| 1            | 358.09                   | 393.54   | 27664880               | 61.36              |
| 2            | 393.54                   | 424.05   | 11504440               | 25.51              |
| 2 3          | 424.06                   | 478.36   | 1799441                | 3.99               |
| 4            | 478.44                   | 555.76   | 2316323                | 5.13               |
| 5            | 555.86                   | 663.78   | 1799441                | 3.99               |
| Hydraulic (  | Gradient (%)             |          |                        |                    |
| 1            | 0.01                     | 3.25     | 37276450               | 68.17              |
| 2            | 3.25                     | 9.90     | 12544300               | 22.94              |
| 2 3          | 9.91                     | 20.43    | 2156892                | 3.94               |
| 4            | 20.45                    | 32.32    | 1862401                | 3.41               |
| 5            | 32.33                    | 62.43    | 844884.2               | 1.55               |
| Saturated T  | hickness (m)             |          |                        |                    |
| 1            | 35.84277                 | 45.09358 | 13360000               | 24.42              |
| 2            | 45.09825                 | 53.95136 | 21860000               | 39.96              |
| 3            | 53.96689                 | 66.08061 | 8322500                | 15.21              |
| 4            | 66.08842                 | 81.07376 | 6005000                | 10.98              |
| 5            | 81.08453                 | 98.28699 | 5162500                | 9.44               |
| Flow veloc   | ity (m/d)                |          |                        |                    |
| 1            | 0.033031                 | 4.699921 | 37190000               | 68.75              |
| 2            | 4.706436                 | 13.66623 | 11750000               | 21.72              |
| 3            | 13.87682                 | 28.57493 | 2020000                | 3.73               |
| 4            | 28.78451                 | 46.18502 | 1910000                | 3.53               |
| 5            | 46.61687                 | 84.14056 | 1220000                | 2.25               |
| Flow disch   | arge (m <sup>3</sup> /d) |          |                        |                    |
| 1            | 330.3056                 | 46999.21 | 37190000               | 68.75              |
| 2            | 47064.36                 | 136662.3 | 11750000               | 21.72              |
| 3            | 138768.2                 | 285749.3 | 2020000                | 3.73               |
| 4            | 287845.1                 | 461850.3 | 1910000                | 3.53               |
| 5            | 466168.7                 | 841405.7 | 1220000                | 2.25               |



**Table: 9.** Parameters for remediation using air injection and vapor extraction in a Carabobo State aquifer, Venezuela

| 1 / 1                  | 15005   |
|------------------------|---|
|                        | 15837   |
|                        | 1.204   |
|                        | 13153   |
| g/mol                  | 78.11   |
| m³/s                   | 49805   |
| m                      | 46  |
| kg/s-m <sup>2</sup>    | 1083  |
|                        | 0.04  |
|                        |   |
| $m^3/d$                | 5075  |
|                        |   |
| kg/d                   | 557.31  |
|                        | 1.204   |
| m <sup>3</sup> /d      | 462.88  |
| g/mol                  | 92.13   |
| $m^3/s$                | 49805   |
| m                      | 46  |
| kg/s-m <sup>2</sup>    | 1083  |
| kmol/s.m <sup>3</sup>  | 0.04  |
| (kmol/m <sup>3</sup> ) |   |
| $m^3/d$                | 6.28  |
|                        |   |
| kg/d                   | 0.156   |
| kg/m <sup>3</sup>      | 1.204   |
| $m^3/d$                | 0.129   |
| g/mol                  | 106.16  |
| $m^3/s$                | 49805   |
| m                      | 46  |
| kg/s-m <sup>2</sup>    | 1083  |
| kmol/s.m <sup>3</sup>  | 0.04  |
| (kmol/m <sup>3</sup> ) |   |
| m <sup>3</sup> /d      | 0.036   |
|                        | m³/s m kg/s-m² kmol/s.m³ (kmol/s.m³ (kmol/m³) m³/d  kg/d kg/mol m³/s m kg/s-m² kmol/s.m³ (kmol/m³) m³/d  kg/d kg/mol m³/s m³/d kg/mol m³/s |

## **DISCUSSION OF RESULTS**

The analysis of physical characteristics indicates that the contamination with hydrocarbons is occurring in the northern region of the La Guacamaya aquifer implying that the contaminants might be transported toward downstream of the aquifer causing a potential great impact on the water for human consumption and industrial uses. The condition of the confined aquifer due to the alternating layers of low plasticity clay with well graded sand has avoided that hydrocarbons in the soil reach upper values to the environmental regulation. In case of hydrocarbon tests in soils, the TPH-GRO (C<sub>6</sub>-C<sub>10</sub>) measured in PM-5 in a maximum magnitude is of 142 mg/kg of soil for a depth varying between 6 and 6.5 m, it has been found below to the generic limits based on the risk dictated by the Environmental Ministry (2006) in Colombia; which is 1000 mg/kg. In the case of Lead measured in PM-4 in a maximum magnitude of 129 mg/kg of soil for a depth varying between 1.5 and 2.0 m, it has been found below to the generic limits based on the risk dictated by EPA, (1997); which is 530 mg/kg.

In the case of BTEX, Benzene measured in PM-6 has a maximum magnitude of 1.234 mg/kg of soil for a depth varying between 4.5 and 5.0 m, it has been found below to



the generic limits based on the risk dictated by Ministry of Space Planning and Environment, Department of Soil Protection, Dutch Standard (2014); which is 2 mg/kg. In the case of Toluene measured in PM-6 in a maximum magnitude of 2.072 mg/kg of soil for a depth varying between 4.5 and 5.0 m, it has been found below to the generic limits based on the risk dictated by Ministry of Space Planning and Environment, Department of Soil Protection, Dutch Standard (2014); which is 50 mg/kg. In the case of Ethylbenzene measured in PM-5 in a maximum magnitude of 1.097 mg/kg of soil for a depth varying between 6.0 and 6.5 m, it has been found below to the generic limits based on the risk dictated by Ministry Space Planning Environment. Department Protection, Dutch Standard (2014); which is 130 mg/kg. In the case of m.Xylene measured in PM-5 in a maximum magnitude of 2.614 mg/kg of soil for a depth varying between 6.0 and 6.5 m, it has been found below to the generic limits based on the risk dictated by Ministry of **Planning** and Environment. Space Department of Soil Protection, Dutch Standard (2014); which is 50 mg/kg. In the case of o.Xylene measured in PM-5 in a maximum magnitude of 0.978 mg/kg of soil for a depth varying between 6.0 and 6.5 m, it has been found below to the generic limits based on the risk dictated by Planning Ministry of Space and Environment, Department of Soil Protection, Dutch Standard (2014); which is 50 mg/kg. In the case of MTBE measured in PM-6 and PM-12 in a maximum magnitude of 3.281 mg/kg of soil for a depth varying between 4.5 and 5 m, it has been found below to the generic limits based on the risk dictated by EPA (2009); which is 39 mg/kg.

In case of hydrocarbon tests in water, the TPH measured in PM-2 (0.8 mg/l), PM-3 (0.4 mg/l), PM-4 (0.9 mg/l), PM-6 (2.3

mg/l), PM-8 (0.4 mg/l), PM-9 (0.7 mg/l), PM-10 (0.4 mg/l), PM-13 (0.6 mg/l), PM-15 (0.5 mg/l), it has been found upper to the generic limits based on the risk dictated by the Ministry of Environment, Housing and Sustainable Development. Colombia (in drinking water); which is 0.32 mg/l. In case of hydrocarbon tests in water, the TPH-GRO measured in PM-1 (275.4 mg/l), PM-5 (76.4 mg/l), PM-6 (210.2 mg/l), PM-9 (19.006 mg/l), PM-10 (679.14 mg/l), PM-11 (275.39 mg/l), PM-14 (6.92 mg/l), it has been found upper to the generic limits based on the risk dictated by the Environmental Ministry (2006)Colombia; which is 4 mg/l. In the case of Lead measured in PM-1 to PM-15 in a maximum magnitude of 0.01 mg/l of water, it has been found upper to the generic limits based on the risk dictated by Ministry Space of Planning and Environment, Department Soil of Protection, Dutch Standard (2014); which is 75 mg/l.

In the case of BTEX measured in water, Benzene measured in PM-1 (23945 µg/l), PM-5 (8.2 µg/l), PM-6 (13000 µg/l), PM-9 (4582 µg/l), PM-10 (36760 ug/l), PM-11 (30270 ug/l), it has been found upper to the generic limits based on the risk dictated by the Sanitary Standard for Drinking Water Quality, Official Gazette Venezuela. N° 36395 Art. 14, which is 10 ug/l. In the case of Toluene measured in PM-1 (19715  $\mu$ g/l), PM-5 (1180  $\mu$ g/l), PM-9 (784 µg/l), PM-10 (44850 µg/l), PM-11 (38900 µg/l), it has been found upper to the generic limits based on the risk dictated by the Sanitary Standard for Drinking Water Quality, Official Gazette Venezuela. N° 36395 Art. 14, which is 700 μg/l. In the case of Ethylbenzene measured in PM-1 (2145 µg/l), PM-5 PM-9 (518  $\mu$ g/l), PM-10  $(1340 \mu g/l),$  $(1690 \mu g/l)$ , PM-11 (5130  $\mu g/l$ ), it has been found upper to the generic limits



based on the risk dictated by the Sanitary Standard for Drinking Water Quality, Official Gazette Venezuela. Nº 36395 Art. 14, which is 300 µg/l. In the case of m.Xylene measured in PM-1 (14065 µg/l), PM-5 (6120 µg/l), PM-9 (5998 µg/l), PM-10 (1123  $\mu$ g/l), PM-11 (1123  $\mu$ g/l), it has been found upper to the generic limits based on the risk dictated by the Sanitary Standard for Drinking Water Quality, Official Gazette Venezuela. Nº 36395 Art. 14, which is  $500 \mu g/l$ . In the case of o.Xylene measured in PM-1 (3965 µg/l), PM-9 (824  $\mu$ g/l), PM-10 (4580  $\mu$ g/l), PM-11 (4830 µg/l), it has been found upper to the generic limits based on the risk dictated by the Sanitary Standard for Drinking Water Quality, Official Gazette Venezuela. Nº 36395 Art. 14, which is 500 In the case of MTBE measured in  $\mu g/l$ . PM-1 (208600 µg/l), PM-5 (58920 µg/l), PM-6 (177180 µg/l), PM-9 (5522 µg/l), PM-10 (570593µg/l), PM-11 (115380 μg/l), PM-12 (21 μg/l), PM-14 (5430 it has been found upper to the  $\mu g/l)$ , generic limits based on the risk dictated by EPA (1997), which is  $20 \mu g/l$ .

The spatial prediction models indicate to the PM-4 and PM-12 as the source of contamination of soil by TPH and congeners and Lead. In all cases, the spatial prediction is explained by a local polynomial interpolation with order 3. The gradient of linear regression function varies between 0.28 and 0.94. The spatial prediction models indicate to the PM-6, PM-13 and PM-15 as the source of contamination of soil by BTEX and MTBE. In all cases, the spatial prediction is explained by a local polynomial interpolation with order 3. The gradient of linear regression function varies between 0.34 and 0.94.

The spatial prediction models indicate to the PM-6, PM-7 and PM-15 as the source of contamination of water by TPH and congeners and Lead. In all cases, the spatial prediction is explained by a local polynomial interpolation with orders 2 and 3. The gradient of linear regression function varies between 0.27 and 0.57. The spatial prediction models indicate to the PM-6, PM-13 and PM-15 as the source of contamination of water by BTEX and MTBE. In all cases, the spatial prediction is explained by a local polynomial interpolation with orders 2 and 3. The gradient of linear regression function varies between 0.41 and 1.44.

respect With to the proposal of remediation applying air injection and vapor extraction, the benzene is the component, which requires the greatest demand of air and generates the greatest amount of vapor by comparing to the estimations of these parameters for the Toluene and o-Xylene in water. For the Benzene, the required air is 13153 m<sup>3</sup>/d (323 cfm) and the vapor extraction is 5075  $m^3/d$  (125 cfm).

## **CONCLUSIONS**

The contamination with hydrocarbons is occurring in the northern region of an aquifer of the Carabobo State implying that the contaminants might be transported toward downstream of the aquifer causing a potential great impact on the water for human consumption and industrial uses. The condition of the confined aquifer due to the alternating layers of low plasticity clay with well graded sand has avoided that the hydrocarbons in the soil reach upper values to the environmental regulation. In the case of water, the contamination with hydrocarborns is upper to the environmental regulation.

In general, in both soil and water, the spatial prediction of hydrocarbons is explained by a local polynomial interpolation whose order varies between 2 and 3, and in a smaller proportion by the global interpolation whose order varying



between 2 and 3. The Kernell functions used are Exponential, Gaussian, Epanechnikov and Quartic. The gradient of linear regression function varies between 0.34 and 0.94, resulting in a moderate to excellent adjustment.

The proposal of remediation consists of applying air injection and vapor extraction, being the required air of 13153 m<sup>3</sup>/d (323 cfm) and the vapor extraction of 5075 m<sup>3</sup>/d (125 cfm).

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